ABB MEASUREMENT & ANALYTICS | WHITE PAPER

Fiber-based FT-NIR analyzer configuration for crude oil analysis

FT-NIR process analysis

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1. Introduction

FT-NIR spectroscopy provides multi-component analysis of physical and chemical properties through a single measurement: the infrared absorbance spectrum. It enables multi-property determination on a complex sample or mixture. NIR technology is widely used in modern refineries as well as in other industries, including food, chemical, pharmaceutical and semiconductor. ABB has successfully and extensively applied FT-NIR technology in final product blending and to various conversion/upgrading process units within the refinery to provide fast and accurate multi-property analysis.

FT-NIR analyzers can also be used for crude oil analysis, offering real-time data on crude oil composition before it enters the crude distillation unit (CDU), allowing feedback for control and optimization, replacing the expensive and time-consuming laboratory methods for crude oil assays (1) (2) (3). An online pre-distillation analysis for crude qualities represents the next step in refiners' efforts to maximize refinery margins. Essentially, the FT-NIR solution discussed herein enables proactive process adaptability to the crude distillation unit (CDU), instead of reactive planning or process modifications caused by outdated or even non-existent crude assay data.

Compared to blend products, crude oil's hydrocarbon composition is complex. Depending on the source, the proportion of the different hydrocarbons can vary dramatically, including its API gravity, sourness and impurities content (i.e., water and particulate matter). A major challenge for refineries is that crude oil quality is not consistent, even if it originates from the same source (or same well). Furthermore, most refineries obtain their crude from a variety of global sources.

There are two key aspects required for successful measurement by FT-NIR:

1. Cost-effective sample conditioning system (SCS) to ensure compatible, representative and timely introduction of the sample to the analyzer for optimal measurement.
2. Optical configuration of the analyzer to ensure reliable spectroscopy measurement of near-infrared absorbance of crude samples.

This paper focuses on the second aspect: the FT-NIR optical configuration. The optical configuration depends on the ideal spectral range for gathering spectroscopic information about crude properties (i.e., combination vs overtone region), as well as careful selection of optical hardware to minimize residual absorption and light loss, which could be detrimental.

2. Spectroscopy and spectral range for analysis – combination versus overtone band regions

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01 Kerosene FT-NIR spectrum measured on an ABB MB3600 using an InAs 3.0 TEC detector and a 1.0 mm pathlength liquid cell
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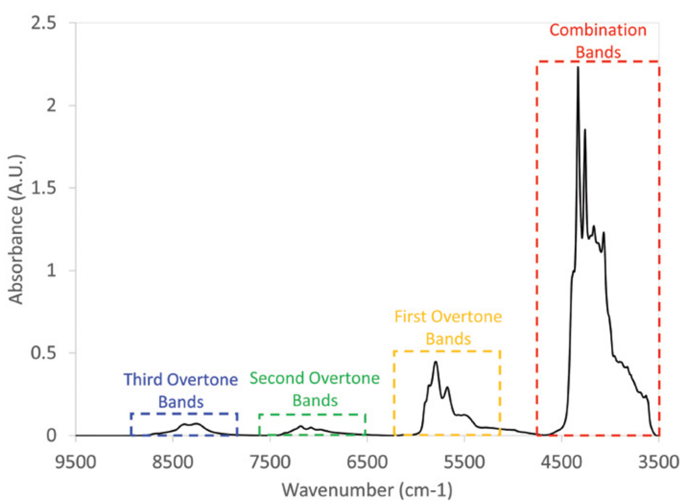
02 Crude darkness impact on the overtone baseline tilt, measured on a MB3600 using an InAs 3.0 TEC detector and a 2.0 mm path-length liquid cell

Infrared (IR) molecular measurement or IR spectroscopy can be achieved through three types of IR peaks: fundamentals, combinations and overtones. While fundamental IR absorption offers inherently intense peaks due to their high molecular absorption cross section, they mainly occur in the mid-IR spectral range where it is less practical for process measurement because they require an extremely small optical path length (< 0.5mm).

Process analysis using an FT-NIR analyzer is typically limited to either the combination spectral region[1], between 4000 and 4800 cm^{-1}, or the overtone region, between 5240 and 9500 cm^{-1}. In this spectral range, the path length becomes more manageable with 0.5 mm used in the combination band region and 2.0 mm for the overtones.

Between these two, the best spectral domain for accurate and reliable hydrocarbon analysis lies in the combination region band. This spectral region possesses inherently sharper and higher molecular detail because they originate from a vibrational combination of the fundamental transition, as illustrated with the kerosene example in Figure 1.

Furthermore, combination bands are less susceptible to residual absorption from the visible spectral region (i.e., resulting baseline tilt) often found in the overtone band regions, as shown in Figure 2. This tilt phenomenon is caused by the inherent crude oil color resulting from the presence of heavy hydrocarbons (e.g., asphaltene), metals and sulfur. As shown in Figure 2, a direct correlation between the crude API gravity (i.e., density) and the severity of the tilt can be observed. The heavier or more dense the crude, the more susceptible it becomes to this adverse effect.



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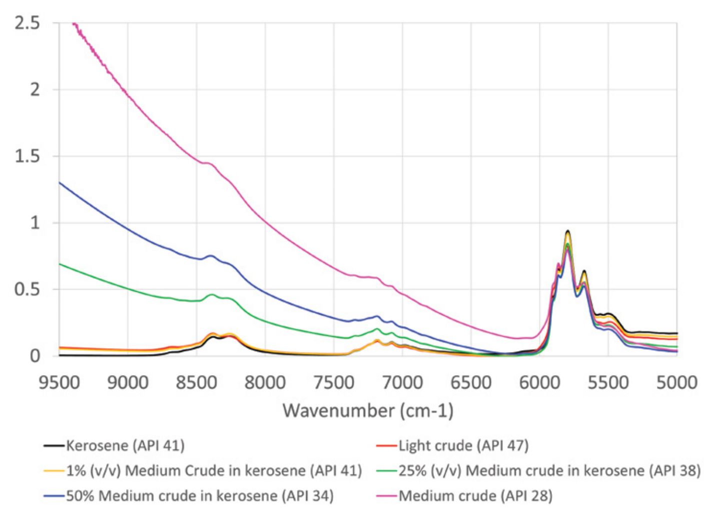

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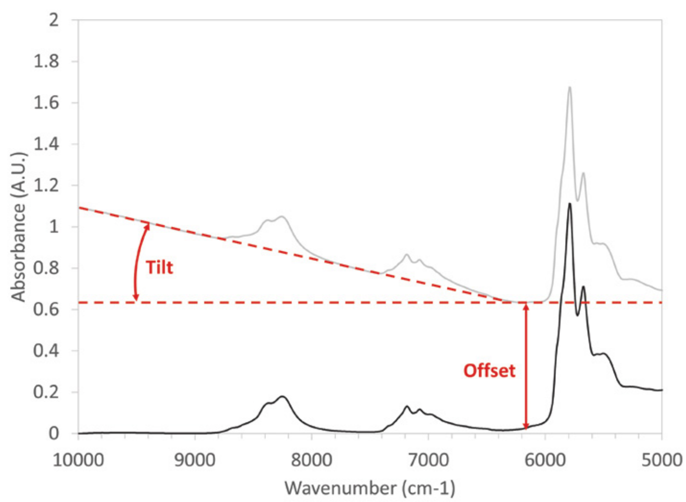
[1] Combination bands lie between mid-IR and NIR but are generally considered to be in the NIR spectral region and the main driver of optical configuration (detector, optical materials, source, etc). Depending on the literature source, combination bands may be defined as being part of the mid-IR spectral region.

Additionally, the presence of baseline tilt and offset, as illustrated in Figure 3, can occur from solid particulates and emulsified water in the crude. Consequently, FT-NIR analysis in the overtone region can quickly become unusable due to these phenomena. Such tilts and/or offsets represent very significant energy losses as well as major absorbance band distortions upsetting subsequent analysis by modeling.

Mathematical corrections of the baseline can be implemented in the spectra pretreatment, including the prediction model, to compensate for the offset and tilt. Nevertheless, if these phenomena are excessive in absorption, they can cause an increase in the overall noise due to loss of light transmission, thus causing a signal-to-noise ratio reduction resulting in noisy or poor measurement quality. If the offset and tilt exceed the range included in the model, predictions are also at risk of being inaccurate.

Additionally, due to the inherent crude oil quality, measurement in the overtone region would be limited to the first overtone band located between 5240 and 6280 cm^{-1}, as shown on Figure 1, to avoid most of the baseline tilt's adverse effect. Ultimately, this would result in a loss of potential information that could render the prediction model inaccurate and unreliable. For the reasons discussed herein, ABB recommends using the combination spectral range for FT-NIR crude oil analysis.



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03 Baseline offset vs tilt effect on crude oil first overtone spectral range

3. Optical hardware selection

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04 FT-NIR detectors light sensitivity, normalized, in the combination spectral range
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05 FT-FT-NIR detectors signal-to-noise ratio in the combination spectral range – the noise standard deviation was measured between 2000-2500 cm^{-1}

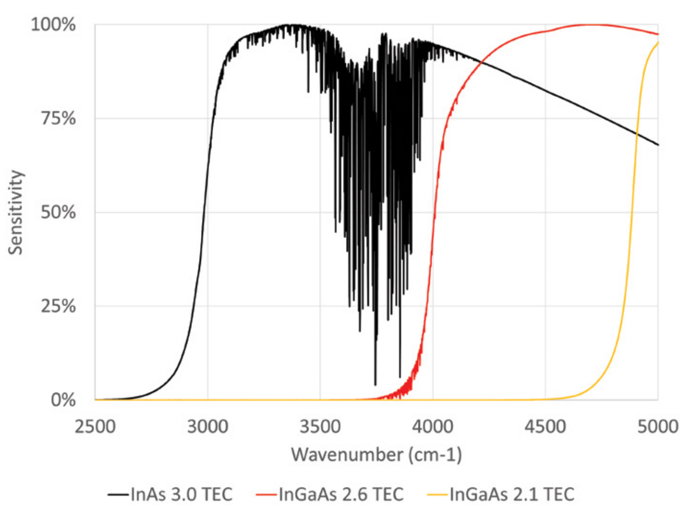
In theory, the combination region is certainly the ideal spectral range for FT-NIR crude oil analysis as it is less susceptible to residual absorption as in the overtone region. However, the quality of the spectrum is not only dependent on the absorptivity of the crude, but also on the optical hardware configuration, most specifically the detector, the cell optical windows material and the fiber optic performance.

3.1 NIR detectors

Measurement in the NIR spectral region for process analysis is generally achieved using three different types of detectors[2]: InAs 3.0, InGaAs 2.6 and InGaAs 2.1. Still, for measurement in the combination region, only the InAs 3.0 detector shows good light sensitivity across the range, as illustrated in Figure 4. Despite the InGaAs 2.6 detector having the potential for use as demonstrated in Figure 5, where its signal-to-noise ratio between 4000 to 4800 cm^{-1} is equivalent to the InAs detector, its 50% cutoff is too close to the spectral range of interest. Consequently, absorption near 4000 cm^{-1} would be at risk of significant intensity variation caused by thermal and vibrational variations.

3.2 Fiber optics

The most common type of fiber optic offered on the market for FT-NIR applications is unambiguously low OH silica (SiO_2) fibers, as they offer long length at relatively low cost while presenting good transmission for NIR spectroscopy. For this reason, measurement in the overtone using fiber-based FT-NIR process analyzer coupled with silica (SiO_2) fiber optic cables have gained increased interest for light hydrocarbon process analysis (e.g., gasoline, diesel, naphtha, kerosene, etc.) in refineries due to their relatively low cost and for integration versatility. Such configuration allows the analyzer to be located hundreds of meters away from the measurement point (i.e., flowthrough cell optics) while also being cheaper than extractive systems where the sample must be brought directly to the analyzer.



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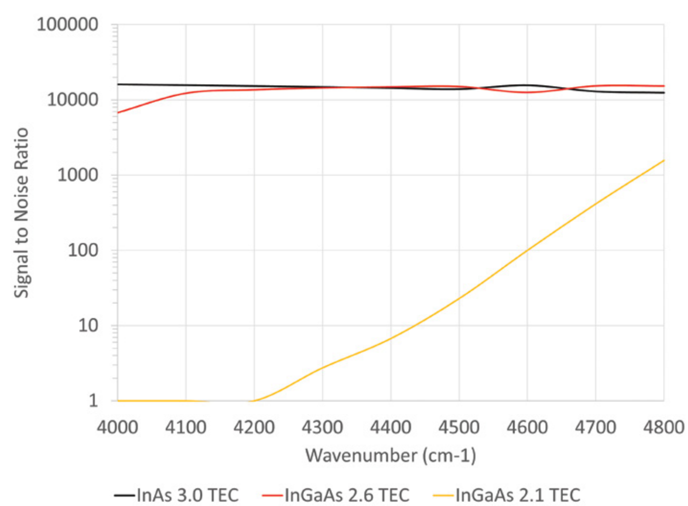

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[2] IR sensitive detectors are often defined by their chemical composition (e.g., InAs for Indium Arsenide, or InGaAs for Indium Gallium Arsenide) followed by their 50% cutoff value expressed in wavelengths (i.e., units of µm).

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06 Fiber optic light transmissivity, normalized, in the combination region, measured with an InAs 3.0 TEC detector, depending on fiber length (Fiber Material_Core Diameter_Length)
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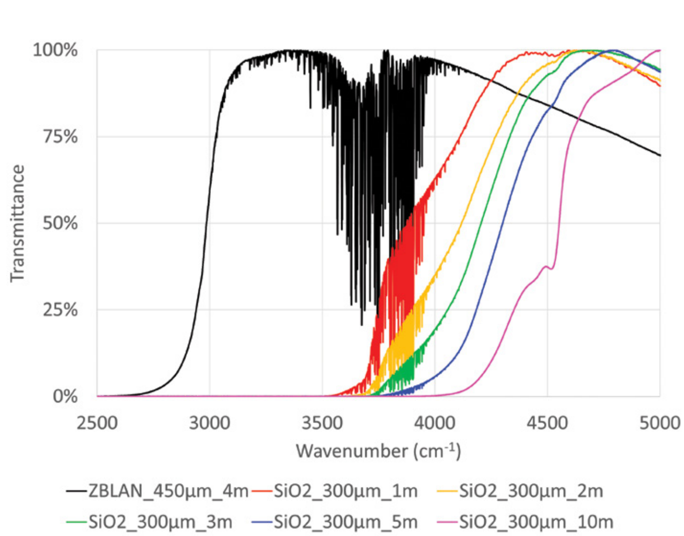
07 Sapphire and BK7 windows transmissivity, normalized, in the combination region

In the first overtone region, the length of low OH silica fiber optic cables have little to no impact on the quality of the spectrum as they provide excellent light transmissivity in that spectral range. However, in the combination region, the fiber length can significantly impact the ability to produce a reliable measurement due to light scattering, bending, interface inhomogeneities and cumulative absorption (e.g., from OH ions) as the length increases. As shown in Figure 6, at more than two-meters in length, the transmissivity of the NIR light below 4500 cm^{-1} falls under 25%. Even if the one-meter fibers can transmit light above 50% in the entire combination range, its length is too short to be practical compared to the two-meter length.

Alternatively to silica fibers, ZBLAN[3] fibers, also commonly referred to as ZrF_4 (zirconium fluoride), can offer improved light transmissivity in the combination region. This type of fiber is notably more expensive and also cannot be manufactured as long as silica fibers due to their brittleness. Still, the ZBLAN fibers provide good light transmissivity covering the combination band region at a length greater than two meters[4].

3.3 Flow cell windows

If we disregard the instrument internal optical system (e.g., interferometer, beam splitter and lenses), the last optical component present in the optical path for fiber-based FT-NIR process analysis is the sample cell window materials used to pass modulated light through the sample with a fixed path length. Typical materials used in ABB's NIR flowthrough cells are either sapphire or BK7 (borosilicate glass). As shown in Figure 7, both exhibit excellent light transmissivity in the combination region, making them suitable for crude oil application. Furthermore, both materials exhibit excellent chemical resistance to acids including hydrogen sulfide and sour gas. However, between the two materials, sapphire is harder than BK7, which would render it more resistant to scratches and wear. Considering the potential for high content of fine-to-ultrafine particulate in the stream, use of sapphire windows could prevent premature wear, which could negatively impact performance over time.



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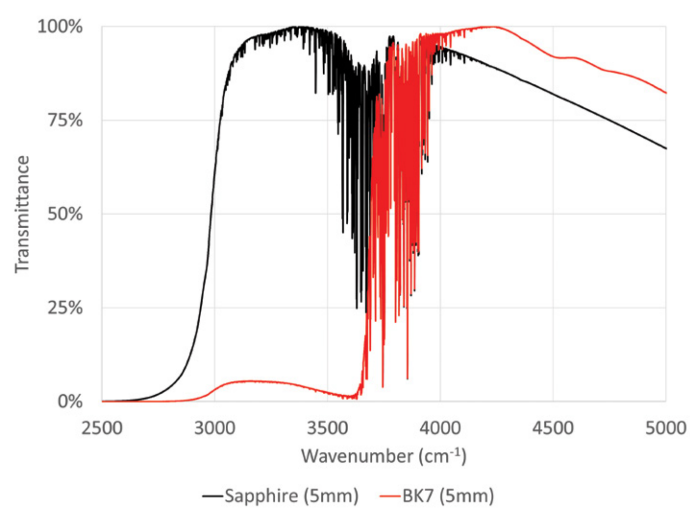

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[3] ZBLAN is the most stable subcategory of heavy metal fluoride glass that is typically made of 53% ZrF_4, 20% BaF_2, 4% LaF_3, 3% AlF_3 and 20% NaF.
[4] Typical ZBLAN fibers can be sold commercially at a maximum of four or five meters in length.

08 Fiber-based FT-NIR process analysis light transmission optical path, from light source to detector, with connection points highlighted

09 Light transmissivity, normalized, in the combination region of different combinations of fiber (type and length) flow cell windows, and analyzer type (MB36000 vs FTPA2000-260) using an InAs TEC detector

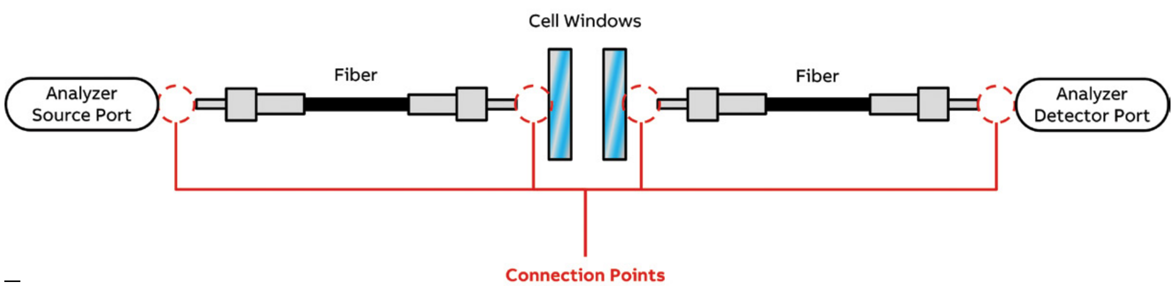
3.4 Full optical path

Identifying and selecting the proper optical materials is crucial, while selecting materials solely based on their individual performance is not recommended. For example, when optical materials are combined, the cumulative residual absorption and loss of light transmissivity caused by the connection points between the different hardware can induce significant loss in light transmissivity. In fiber-based FT-NIR process analysis, the light must travel through two fibers and two windows before going back to the analyzer, which involves at least four transmission and connection points susceptible to light loss due to misalignment, as illustrated in Figure 8.

Testing done by combining different fiber types (ZBLAN and silica) and lengths (1, 2, 3, 4 and 5 meters) with different window materials (sapphire and BK7) using an InAs 3.0 TEC detector, as seen in Figure 9, demonstrated that these optical combinations have significant impact on performance. Even though BK7 windows have great light transmissivity when combined with SiO2 fibers, the transmittance significantly drops between 4250 cm^{-1} and 4500 cm^{-1}, compared to the same configuration but with sapphire windows. On the other hand, ZBLAN fibers combined with either sapphire or BK7 windows show better transmissivity in the combination region where optimal measurement is made.

When considering the analyzer's internal optic components, it is clear that the use of a BK7 beam splitter and fiber launcher as found in ABB's FTPA2000-260 analyzer significantly limits the light transmissivity in the lower range of the combination region. For this reason, the use of ZnSe optics or equivalent are preferable because it would lower the 50% cutoff and improve the overall light transmissivity in the spectral range of interest (i.e., the combination band region).

Analysis of the optical material light transmissivity has demonstrated that ZBLAN fibers of at least four or five meters in length combined with an InAs detector and either BK7 or sapphire (preferably) flow cell windows are necessary to achieve optimal measurement performance in the combination region while providing minimal fiber length for integration in refinery process analysis.



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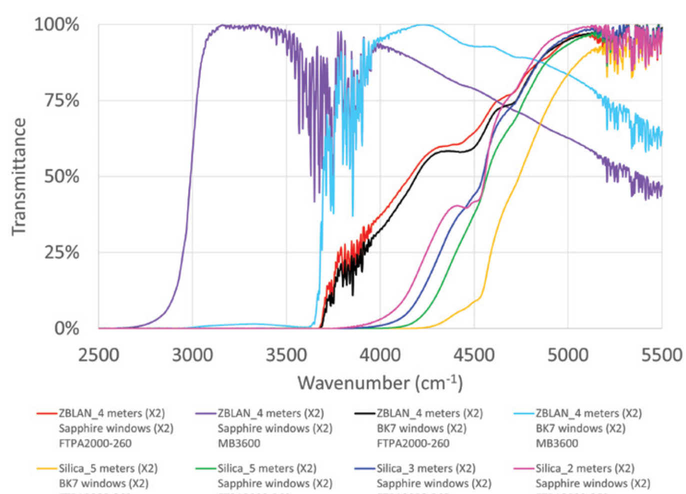

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[5] $ZCaF_2$ or BaF_2 (50% cutoff at 3000 cm^{-1} for both).

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10 Premium gasoline signal-to-noise ratio in the combination region depending on system optical configurations
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11 Medium crude oil signal-to-noise ratio in the combination region depending on system optical configurations

3.5 Crude oil measurement performance
Performance of crude oil spectrum measurement in the combination region was obtained by measuring the spectrum quality in terms of the signal-to-noise ratio using medium crude oil compared to premium gasoline as a reference. These measurements were achieved using an ABB MB3600 and FTPA2000-260 analyzer equipped with different detectors (i.e., InAs 3.0 TEC and InGaAs 2.6 TEC) and using different fiber optic materials and lengths, as well as different flowthrough cell window materials. Both fluids were preconditioned at 40°C and manually injected into the flowthrough sample cell. Ten consecutive spectral measurements were performed at a resolution of 4 cm^{-1} and 50 scans each.

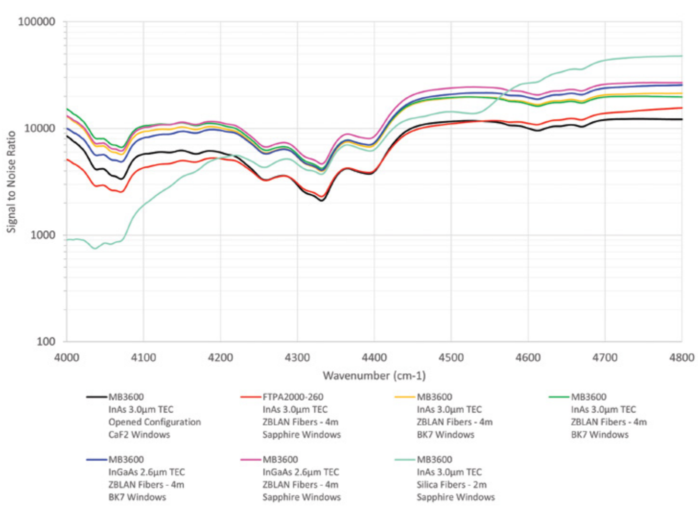
The signal-to-noise ratio (SNR) of the normalized single beam spectra was calculated over the entire combination range (4000 – 4800 cm^{-1}) divided by the noise signal variation between 2000 and 2500 cm^{-1}. The SNR results for premium gasoline and medium crude oil are shown in Figure 10 and Figure 11 respectively.

According to the results, it is clear that an FT-NIR analyzer that uses BK7 internal optics provides significantly lower signal-to-noise ratio, about half the performance, compared to uses of ZnSe or equivalent components.

In terms of fiber types, despite providing good SNR performance in the upper range of the combination region, silica fibers are underperforming in the lower range that is about four times less performant than using ZBLAN fibers.

Regarding the use of either BK7 or sapphire cell windows, the results showed no significant SNR performance differences when combined with ZBLAN fibers and either the InAs 3.0 µm or InGaAs 2.6 µm detectors. However, as mentioned in the above section, use of sapphire cell windows could provide increased durability over time.

Lastly, despite being more suitable for IR combination bands, the InAs detector performance was tested against the InGaAs 2.6 µm detector to see if the former actually provided increased performance. By comparing of the results, for both premium gasoline and medium crude oil, no significant difference is noted between the use of either detector. However, InAs 3.0µm could prove to be more stable against changes in temperature and vibration because its 50% cutoff is well below 4000 cm^{-1}.



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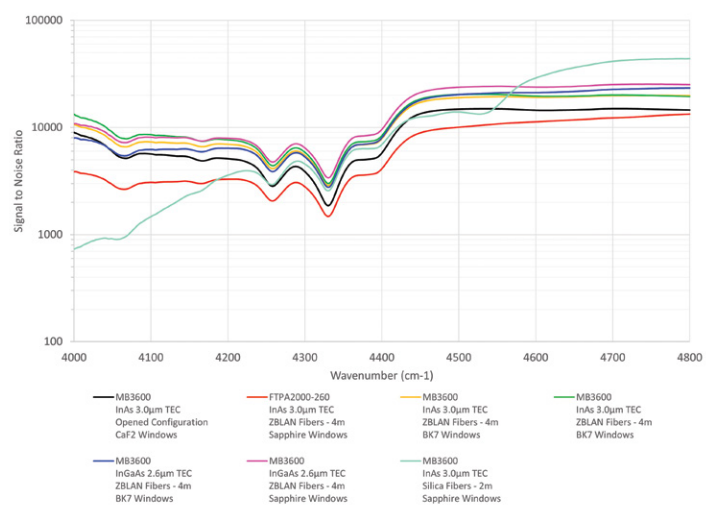

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4. Analyzer configuration

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12 CDU input and output streams configuration using the multichannel FT-NIR process analyzer
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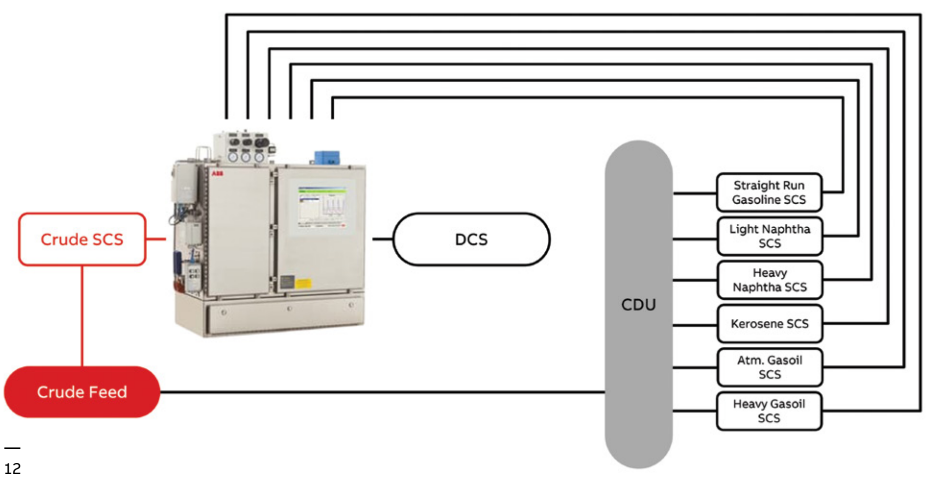
13 CDU input and output streams FT-NIR parameters

Online FT-NIR process measurement of crude oil in the combination region can be achieved using a fiber-based FT-NIR process analyzer equipped with an InAs detector, sapphire windows (preferably), internal components made of ZnSe or equivalent material, and the use of ZBLAN fibers. However, because of the short length of the ZBLAN fibers, the crude sampling conditioning system must be positioned close to the analyzer, thus placing physical distance limits for integration as well as the need for sample crude to be brought close to the analyzer location.

The measurement of crude oil is obviously important and the focus for optical configuration herein. The crude oil coming in as feed to the CDU can have dramatic impacts to the downstream process units as well as to achieve final product targets within the refinery. Additional measurements that come after the CDU are also possible to ensure the CDU cuts are known.

The use of a multichannel fiber-optic multiplexed analyzer for which separate and different detectors can be assigned to individual sample streams, such as with the ABB FTPA2000-HP260X FT-NIR analyzer, allows measurement of one or two feeds of crude and up to six or seven other hydrocarbon streams simultaneously (for a total of eight measurement streams). Such configuration would allow using the instrument to measure both the input and output streams of the crude oil distillation unit (CDU), as illustrated on Figure 12. The crude SCS for the CDU feed stream can still be located near the analyzer, to meet the fiber length limitation, while the remaining CDU output product streams can be relayed at greater distances using silica fibers, since these streams are not required to be measured in the combination region, as shown in Figure 13.



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Stream	Optical channel	Spectral range (cm⁻¹)	Fiber type	Fiber length (m)	Detector type	Path length (mm)	Temperature (°C)
Crude	1 and 2	4000 – 4800	ZBLAN	4 or 5	InAs 3.0	0.5	40
Straight-run Gasoline	3	5500–9500	Low OH silica	Up to 300	InGaAs 2.1	2.0	25
Light Naphtha	4	5500–9500	Low OH silica	Up to 300	InGaAs 2.1	2.0	25
Heavy Naphtha	5	5500–9500	Low OH silica	Up to 300	InGaAs 2.1	2.0	25
Kerosene	6	5500–9500	Low OH silica	Up to 300	InGaAs 2.1	2.0	25
Atm. Gasoil	7	5500–9500	Low OH silica	Up to 300	InGaAs 2.1	2.0	75
Heavy Gasoil	8	5500–9500	Low OH silica	Up to 300	InGaAs 2.1	2.0	75

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5. Conclusion

The use of FT-NIR technology to perform accurate determination of several crude oil attributes revolutionizes traditional monitoring solutions for refiners, enabling fast crude oil measurement to allow feedback and control. Still, reliable predictions and efficient performance cannot be achieved without using proper optical materials and configuration.

This paper demonstrates that FT-NIR process measurement of crude oil feed is optimized through the combination spectral band to maximize the information throughput while limiting the impact of residual absorption from the inherent quality of the feed. As compared to measurement in the overtone region, the combination region requires careful selection of the optical components, which also induces system integration limitations.

Nonetheless, by combining an InAs detector with ZBLAN fibers and sapphire flow cell windows, it is possible to achieve satisfactory spectrum performance (i.e., better signal-to-noise ratio), thus unlocking the use of fiber-based FT-NIR process analysis for crude oil application. Furthermore, by including use of a multichannel fiber optic analyzer, simultaneous measurement of the input (i.e., crude) and output streams of the crude distillation unit can be achieved.

It should be mentioned that it is still imperative that the FT-NIR process analyzer be combined with a carefully designed and integrated sampling conditioning system (SCS) to ensure that the crude sample stream meets the minimum requirements for stable FT-NIR measurement.

6. References

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